

THE PREPARATION AND PROPERTIES OF
SOME PLATINUM AMINES

BY

JOHN ARTHUR MATTERN

B.S., Ohio State University, 1941

M.S., University of Illinois, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
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THE PREPARATION AND PROPERTIES OF SOME PLATINUM AMINES

Although it is generally believed that chelating groups such as ethylenediamine are unable to reach across *trans* positions in the coordination sphere of a metal, there is no reason to suppose that a chelating group of sufficient size cannot, under the proper conditions, coordinate across *trans* positions. However, previous attempts to prepare simple chelate rings of seven or more members have given inconclusive or negative results. The general procedure has been to treat a metallic salt or complex with a large diamine, such as pentamethylenediamine, in the hope that both amine groups will coordinate to the metallic ion. This reaction presents difficulties, however. Although there is an excellent chance that one amine group in the course of its motion will encounter and coordinate to a metallic ion, the probability that the second amine group will reach and coordinate to the same metallic ion is rather small because the motion of this second amine group is comparatively unrestricted. Accordingly, one or more of the following reactions takes place instead of chelation: (1) The precipitation of the metal as an insoluble hydroxide (2) the formation of polymer-like materials by coordination of one diamine molecule to two different metallic ions (3) the filling of the coordination sphere with more strongly chelating groups as, for example, the formation of $[\text{Co en}_3]\text{Cl}_3^*$ from $[\text{Co en}_2\text{Cl}_2]\text{Cl}$. Little work has been done to ascertain whether or not these side reactions can be avoided by the use of nonaqueous solvents or the use of catalysis.

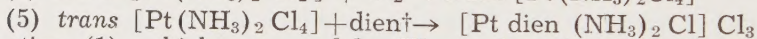
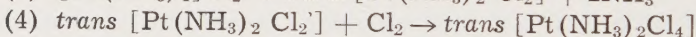
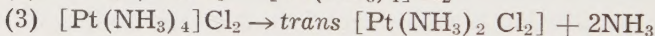
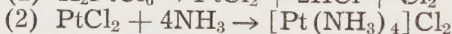
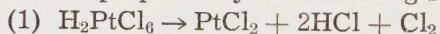
Diethylenetriamine, although its end amine groups are just as far removed from each other as those of pentamethylenediamine, is readily able to place its two end amine groups in *trans* positions of the coordination sphere because coordination of the center amine group greatly restricts the motion of an uncoordinated end group and thereby increases the probability of co-

*Abbreviations used are: en, ethylenediamine; and dien, diethylenetriamine.

ordination. This amine, therefore, coordinates preferentially as a tridentate group. Mann¹, in fact, has found it difficult to prepare a bidentate compound of diethylenetriamine by direct means.

If it is possible to remove the middle amine from the coordination sphere of such a tridentate complex, an eight-membered chelate ring may be produced which spans *trans* coordinate positions. Two possible methods for doing this are: (1) to take advantage of the change of coordination number with change of valence which some metals exhibit and (2) to replace one group with another in the coordination sphere. Chernyaev and Fedorova² used both of these methods to prepare monodentate compounds of ethylenediamine from the corresponding bidentate compounds.

The tridentate compound used in this investigation was 2-chloro-1,6-diammine-3,4,5-diethylenetriamine platonic chloride which was prepared by the following series of reactions:

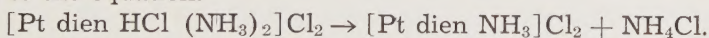


Reaction (1), which was used by Kharasch and Ashford³, was found to be much easier to carry out than reduction by sulfur dioxide or other means. Reaction (2) was improved by the use of Norite charcoal as a catalyst which eliminated troublesome byproducts. Reaction (3) was conducted at 230-240°C. at a pressure of 120-140 mm. of mercury. Reaction (5) was conducted by shaking the theoretical amount of diethylenetriamine with *trans* $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ in the presence of Norite charcoal at room temperature. The use of a higher temperature resulted in reduction to $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and the use of excess amine produced the *bis*-diethylenetriamine complex $[\text{Pt dien}_2]\text{Cl}_4$.

Platinum was chosen for this investigation because (1) coordination compounds of this metal generally show a coordination number of six in the tetravalent state and a coordination number of four in the divalent state and (2) coordination compounds of this metal do not usually show a tendency to rearrange. Assuming that no rearrangement took place which

would involve breaking of the strong platinum-ammonia bond, the diethylenetriamine in $[\text{Pt dien (NH}_3)_2 \text{Cl}] \text{Cl}_3$ has its two end amine groups *trans* to each other and its middle amine group *trans* to a chloride group. There are, therefore, two factors which aid the expulsion of the secondary amine group from the coordination sphere, namely: (1) the *trans* effect and (2) the decreased stability of secondary amine coordinate bonds in comparison with those of primary amines. Moreover, the chloride group, which is not as firmly coordinated to platinum as nitrogen, is also easily expelled from the coordination sphere. Reduction of $[\text{Pt dien (NH}_3)_2 \text{Cl}] \text{Cl}_3$ may, therefore, produce a planar compound containing bidentate diethylenetriamine attached to *trans* positions of the coordination sphere. Rearrangement is not expected in the course of this reaction if the groups which leave the coordination sphere are *trans* to each other.

The reduction of $[\text{Pt dien (NH}_3)_2 \text{Cl}] \text{Cl}_3$ by electrolysis was found to give a mixture which, upon reprecipitation, indicated a N/Pt ratio of 4.6 and a Cl/Pt ratio of 2.6. After the reprecipitation process had been repeated four times these ratios had dropped to 4.1 and 2.1 respectively. Titration of the reduction product of $[\text{Pt dien (NH}_3)_2 \text{Cl}] \text{Cl}_3$ with base showed that approximately one-sixth of the chlorine was present as available hydrochloric acid. This suggests that the reduction product contains both bidentate and tridentate compounds of diethylenetriamine, the former being readily converted to the latter according to the equation:



If the bidentate compound contains primary amine groups joined to *trans* positions of the coordination sphere, this reaction is highly probable.

The reduction product of $[\text{Pt dien (NH}_3)_2 \text{Cl}] \text{Cl}_3$ was found to react readily with hydrochloric acid to produce *trans* dichlorodiammine platinum. Identification as the *trans* form was made by ultraviolet absorption studies and by the preparation of the bis-oxalato derivative $[\text{Pt NH}_3)_2 (\text{HC}_2\text{O}_4)_2]$ according to Grin-

†The diethylenetriamine used in this investigation was obtained from the Carbon and Carbide Chemicals Corporation.

berg⁴. It is difficult to believe that the *trans* dichloro salt would be obtained from a tridentate compound of diethylenetriamine except under very severe conditions. Production from a bidentate compound would require that diethylenetriamine span *trans* positions unless rearrangement takes place.

Further work is needed to ascertain whether or not such a bidentate compound can be isolated in pure form. It is suggested that the use of diethylenetriamine or similar compound containing a somewhat poorer coordinating group in the center may, by the method outlined, prove useful in synthetic work.

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VITA

The author was born at Archbold, Ohio, on July 5, 1919, and received his elementary and high school education in the public schools at Delta, Ohio. He enrolled at the Ohio State University in 1937 from which he received the degree of Bachelor of Science in Chemistry in 1941. From 1941 to 1944 and from 1945 to 1946 he was enrolled in the Graduate School of the University of Illinois and held a teaching assistantship in inorganic chemistry. He received the degree of Master of Science from that University in 1943. During the year 1944-45 he was employed as Special Research Assistant by the Munitions Development Laboratory of the University of Illinois.

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